Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

Quarterly Technical Progress Report

October 1, 2004 – December 31, 2004

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ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-01NT41185, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," during the time-period October 1, 2004 through December 31, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE), and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. Oxidized mercury is removed in the wet FGD absorbers and collected with the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale to provide engineering data for future full-scale designs. The pilot-scale tests will continue for 14 months or longer at each of two sites to provide longer-term catalyst life data.

This is the thirteenth full reporting period for the subject Cooperative Agreement. During this period, only the second pilot unit, at CPS' Spruce Plant, was operated. Operation of the first pilot unit at the GRE Coal Creek site was concluded in the previous quarter. That pilot unit was shipped to TXU Generation Company LP's Monticello Steam Electric Station, for mercury oxidation catalyst testing as part of NETL project DE-FC26-04NT41992. The only project activity related to the Coal Creek test program was the development of preliminary economics for the oxidation catalyst process based on the previously reported results from Coal Creek. These preliminary economics are included in this report.

For the second pilot unit at CPS' Spruce Plant, the oxidation catalyst pilot unit continued in operation throughout the quarter. One catalyst activity measurement trip was conducted, in October, and Ontario Hydro relative accuracy tests were conducted. These results are included in this report.

Testing efforts at Spruce also included pilot wet FGD tests treating flue gas from downstream of the four catalysts. The pilot wet FGD tests were conducted as part of NETL project DE-FC26-04NT41992, and are reported in the current Quarterly Technical Progress Report for that project.

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INTRODUCTION

This document is the quarterly Technical Progress Report for the project "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," for the time-period October 1, 2004 through December 31, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE) and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. The oxidizing species are already present in the flue gas, and may include chlorine, hydrochloric acid (HCl) and/or other species. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with and/or adsorbs on the byproducts from the FGD system. The objective of this project is to test previously identified catalyst materials at pilot scale to provide engineering data for future full-scale designs. The pilot-scale tests will continue for 14 months or longer at each of two sites to provide longer-term catalyst life data. After successful completion of the project, it is expected that sufficient full-scale test data will be available to design and implement demonstration-scale installations of the catalytic mercury oxidation technology.

The two utility team members are providing co-funding, technical input, and host sites for testing. GRE provided the first test site at their Coal Creek Station (CCS), which fires a North Dakota lignite, and CPS is providing the second site at their J.K. Spruce Plant, which fires a Powder River Basin (PRB) subbituminous coal. These two host sites each have existing wet FGD systems downstream of high-efficiency particulate control devices, an ESP at CCS and a reverse-gas fabric filter (baghouse) at Spruce**.**

The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, October 1, 2004 through December 31, 2004, is the thirteenth full technical progress reporting period for the project. During this period, there was no testing at the first pilot unit site, at the GRE Coal Creek Station. For the second pilot unit at CPS' Spruce Plant, the catalyst pilot unit continued in operation throughout the quarter. One catalyst activity measurement trip was conducted, in October, and Ontario Hydro relative accuracy tests were conducted. Also, pilot wet FGD tests were conducted as part of NETL project DE-FC26-04NT41992, and are reported in the Quarterly Technical Progress Report for that project.

The only project effort related to the Coal Creek test program was to develop preliminary economics for the low-temperature mercury oxidation catalyst process, based on the Coal Creek results. These preliminary economics are presented and discussed in this report.

At CPS' Spruce Plant, catalyst activity results were measured during the month of October. These measurements showed that the fabric filter outlet flue gas mercury content is still highly oxidized (~60 to 80%). The relatively low inlet elemental mercury concentrations to the pilot unit (1-4 $\mu g/Nm^3$) make it more difficult to quantify catalyst oxidation activity than at Coal Creek. To improve the accuracy of the mercury oxidation measurements, two newer mercury SCEMs with more sensitive atomic absorption detectors were used to simultaneously monitor the pilot inlet and catalyst outlet locations. The catalyst activity results from this trip indicate 76 to 92% elemental mercury oxidation across three of the four catalysts. The fourth catalyst, the SCR catalyst, showed a much lower oxidation percentage of 41%.

Ontario Hydro measurements were also made during the quarter, simultaneous with the wet FGD pilot tests mentioned above. The intent was for these Ontario Hydro measurements to serve as relative accuracy tests for the Hg SCEM normally used to quantify catalyst mercury oxidation activity. However, failure of a heater on the inertial gas separator filter used in the SCEM sample conditioning system made the corresponding SCEM measurements during the Ontario Hydro runs suspect. Also, due to sampling port configurations on the pilot unit, it was not possible to use two Hg SCEMs to simultaneously monitor catalyst inlet and outlet mercury concentrations during the Ontario Hydro runs. Consequently, one monitor had to be cycled between the catalyst inlet and outlet, and between measuring total and elemental mercury during each Ontario Hydro run. This, along with variability in the pilot unit inlet mercury concentration and speciation at Spruce, made comparison of results from the two methods difficult.

Problems Encountered

There were no significant new problems encountered during the reporting period, other than the technical issues described in Section 4 of this report and mentioned above.

Plans for Next Reporting Period

During the next reporting period (January 1 through March 31, 2005), there will be no further pilot-scale tests conducted at Coal Creek as part of this project. Only reporting activities remain.

Operation of a second oxidation catalyst pilot unit, at CPS' Spruce Plant, will be concluded in early February 2005, at which time end-of-test catalyst activity measurements will be made. A number of in situ catalyst regeneration tests will likely be conducted, depending on which catalysts show measurable loss of activity after the 14 to 15 months they will have been in service at Spruce.

Prospects for Future Progress

During the final reporting period for this project (April 1 through June 30, 2005), no testing is scheduled at either of the two sites, as both pilot units will have been shut down and moved to new sites as part of the 41992 project. The only remaining project effort will be reporting.

EXPERIMENTAL

The work described in this technical progress report was conducted using two different experimental apparatuses. One is an elemental mercury catalyst oxidation pilot unit (8000 acfm of flue gas treated) located at CPS' Spruce Plant in San Antonio, Texas. The pilot unit has four separate compartments that allow four different catalysts to treat flue gas from downstream of the host plant's particulate control device and upstream of its FGD system. Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in previous quarterly technical progress reports[1,2, 3, 4].

The activity of these catalysts is being determined by measuring the change in elemental mercury concentration across each catalyst, while ensuring that the total mercury concentrations do not change significantly across the catalyst. These measurements are primarily being conducted using a mercury semi-continuous emissions monitor (SCEM) developed with funding from EPRI. The analyzer has been described in a previous report[5]. Periodically, the analyzer results are being verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro method.

The second experimental apparatus is a bench-scale test unit that is used to evaluate the activity of candidate catalyst cores under simulated flue gas conditions. However, no bench-scale tests were conducted during the current quarter. The bench-scale catalyst oxidation test apparatus was previously described in quarterly technical progress reports[3, 4].

RESULTS AND DISCUSSION

This section provides details of technical results for the current reporting period, October 1 through December 31, 2004. The technical results presented include preliminary process economics based on data from the first pilot unit at GRE's CCS and results from operation of the second pilot unit at CPS' Spruce Plant.

Preliminary Process Economics Based on Pilot Unit Data from CCS

A primary objective of this test program has been to develop the information required to size catalysts for future full-scale installations, and to determine catalyst life. Both of these are components of the cost of oxidation catalyst technology for enhancing mercury capture in plants that have wet FGD systems. Now that testing is completed at CCS, these data can be used to estimate process costs for a North Dakota lignite application.

The economics were developed for a single, 500-MW plant in North Dakota that fires North Dakota lignite. The required mercury control percentage was based on the minimum specified in NETL solicitation DE-PS26-03NT41718 (Large-scale Mercury Control Technology Field Testing Program – Phase II), 55% for lignite fuels. This percentage represents a mercury removal increase beyond the "baseline" removal for the plant being considered.

The plant was assumed to have a large, cold-side ESP for particulate control, and a wet FGD system for SO_2 control. The wet FGD system was assumed to treat 100% of the flue gas from the unit. Many FGD systems on plants that fire North Dakota lignite currently bypass as much as 25% of the flue gas around the FGD system. However, for this evaluation it was assumed that the anticipated Clean Air Interstate Rule, the recent upswing in SO_2 credit values, and/or other regulatory or economic drivers will lead most scrubbed plants to upgrade to 100% scrubbing, independent of mercury co-removal drivers. Consequently, costs to upgrade an existing FGD system to scrubbing 100% of the flue gas were not included in this evaluation.

The costs for oxidation catalyst technology were compared to projected costs for injecting Norit FGD carbon to achieve the same minimum mercury capture level. A number of assumptions had to be made regarding the base plant before developing these cost estimates, including:

- The flue gas at the ESP outlet contains a minimum of 15% oxidized mercury, with the balance being elemental mercury, although, as at CCS, the oxidation percentage may be higher much of the time;
- The existing ESP is adequately sized to capture activated carbon to maintain particulate emissions compliance;
- No mercury is currently captured with the fly ash in the ESP;
- The wet FGD system will remove a net amount of 90% of the oxidized mercury in the flue gas entering the FGD;
- Carbon injection for mercury capture will not affect the mercury oxidation percentage at the ESP outlet;

- The plant currently sells all of its fly ash (a sensitivity case considers the situation where the plant landfills its fly ash); and
- Fly ash sales would be lost if activated carbon is injected upstream of the ESP for mercury control.

Table 1 summarizes a number of other details that went into the economic analysis.

Table 1. Factors Used to Develop Mercury Control Process Economics

Parameter	Value
Palladium catalyst cost, $/ft^3	$1050
Carbon #6 catalyst cost, $/ft^3	$710 to $880
Catalyst disposal cost, $/ton	$200
Activated carbon cost, $/lb f.o.b. Marshall, Texas	$0.50
Activated carbon delivery cost, $/ton-mi.	$0.15 (1300 miles total)
New plant equipment economic life, yrs	15
New plant equipment capital recovery factor	0.12
Fly ash sales price, $/ton	$4.40*
Landfill disposal cost, $/ton	$3.65**
Process utilities cost	Not estimated
Process operating and maintenance labor	Not estimated

*Value developed from data reported on 2001 EIA-767 form for CCS
**Value reported by CCS plant management

The estimated quantities of catalyst and activated carbon required to achieve an additional 55% mercury removal (or greater) require some discussion. For the catalysts, the minimum 55% additional mercury capture requirement and the assumption of a minimum of 15% oxidized mercury in the ESP outlet flue gas corresponds with a required oxidation percentage across the catalyst of 62%. The resulting overall mercury capture would be 61%.

Since the catalysts were observed to degrade in mercury oxidation activity with time in service, it is likely that sufficient catalyst volume would be installed to exceed this minimum by a substantial margin initially, then gradually degrade to that minimum value. At that point, the catalyst would have to be regenerated or replaced.

The activity versus time data for the palladium and C #6 catalysts presented in the previous quarterly technical progress report[6] were used to develop linear expressions of catalyst oxidation percentage versus time in service. Assuming the catalysts are installed at the same area/space velocity values as in the pilot unit, these linear equations can be used to predict how long each catalyst can be in service while achieving at least 62% elemental mercury oxidation. For both catalysts, the prediction was 720 to 730 days, or approximately two years.

It was decided to treat two years as the effective life of each catalyst type. After two years the catalyst would either have to be replaced or regenerated. Most plants operate no more than two years without taking at least a one- to two-week outage, which should be an adequate amount of time to change out or regenerate catalysts.

For activated carbon, it was assumed that enough carbon would have to be injected such that the sum of the mercury removed by carbon injection and subsequently across the FGD system would equal that of the oxidation catalyst process, or 61%. For the FGD capture assumptions stated above, this equated to 55% mercury capture in the ESP. Based on previous full-scale test results on GRE's Stanton Station Unit 1, which fires a similar lignite, an injection rate in the range of 4 to 6 lb/mmacf of flue gas would be required with FGD carbon to achieve this control level.[7] A mid-point value of 5 lb/mmacf of flue gas was used for these estimates.

Note that this does not result in a completely comparable situation for mercury capture for the two technologies. For the oxidation catalysts, the overall mercury capture would start at about 85% with fresh catalyst, and gradually degrade to 61% after two years, based on 15% mercury oxidation in the ESP outlet flue gas. In comparison, the activated carbon injection case would achieve a consistent 61% capture over this same period, or a significantly lower percentage than the oxidation catalyst cases on average. The mercury capture efficiencies for both technologies would increase when the ESP outlet mercury is more highly oxidized than 15%.

In a "cap and trade" mercury control scenario, the additional time-averaged additional mercury capture with the oxidation catalyst technology (an average of greater than 70% vs.55% with activated carbon) would bring economic benefits to the utility, either by offsetting mercury emissions from other units or potentially through free market emissions credit trading. It might be more equitable to compare the two technologies at the average projected mercury capture percentage for the oxidation catalyst technology rather than at the minimum at the end of the catalyst life cycle.

Base Case Economics

Table 2 compares the projected economics for carbon injection technology to those for the two more active oxidation catalysts at CCS, palladium and C #6. The cases in the table assume that either catalyst would be replaced after two years, with no attempt at regeneration. The annual cost of each process is shown as a "first-year" cost, meaning the operating and maintenance (O&M) costs and catalyst purchase costs are shown in present day dollars and not "levelized" over the economic life of the control system.

Table 2. Comparison of Base Case Economics for Mercury Control Technologies

Parameter	FGD Carbon Injection	Palladium-based Oxidation Catalyst	C #6 Oxidation Catalyst
Capital Equipment, $1000	$2,213	$1,289	$1,289
Catalyst Cost, $1000	-	$5,360*	$5,218**
Delivered Carbon Cost, $1000/yr	$3,109	-	-
Lost Fly Ash Sales, $1000/yr	$1,121	-	-
Increased Landfill Disposal Costs, $1000/yr	$939	-	-
Subtotal O&M Costs, $1000/yr	$5,169	-	-
Capital Equipment Amortization, $1000/yr	$266	$155	$155
Catalyst Amortization Costs, $1000/yr	-	$3,006	$2,926
Total First-year Costs, $1000/yr	$5,435	$3,161	$3,081
First-year Cost, % of Activated Carbon Cost	-	58	57

*Includes delivery, installation, and disposal costs
**Includes delivery, installation, and disposal costs; value shown is based on the low end of the $710/ft^3 to $860/ft^3 projected catalyst cost

The oxidation catalyst cases assume that either catalyst would be disposed of as a hazardous waste. However, it remains to be determined whether the spent catalysts would be classified as a hazardous waste when tested by the toxicity characteristic leaching procedure (TCLP) to determine the concentrations of hazardous metals in the leachate from the tests. TCLP tests are planned on catalyst samples recovered from the pilot unit at CCS. Also, in the case of the palladium catalyst, there exists a significant market for palladium recovery from spent automotive catalysts, so it is possible that spent mercury oxidation catalysts could also be recycled to recover the palladium content. (The spent catalysts would contain between $500,000 and $1 million worth of palladium at current prices).

The comparisons in Table 2 show that even when considering replacing the catalysts every two years, the oxidation catalyst technology can be about 40% less costly than activated carbon injection based on the assumptions described above. It is interesting to note that, although the experimental carbon used to make the C #6 catalyst is three orders of magnitude less costly than palladium on a mass basis, this lower raw material cost does not significantly lower the estimated cost of the C #6 catalyst technology. In fact, the installed C #6 catalyst costs would be greater than the installed cost of palladium-based catalyst if the high end rather than the low end of the cost estimate range for the carbon catalyst were used for this comparison ($860/ft^3 vs. $710/ft^3).

There appears to be two reasons why the C #6 catalyst is nearly as expensive as the palladium catalyst. One is that, based on the CCS results, it is estimated to take a greater quantity of the C #6 catalyst to equal the performance of palladium. The other is that the estimated production costs for the experimental carbon catalyst negate much of the expected benefit of the lower raw catalyst material cost, when expressed in dollars per cubic foot of catalyst produced. The raw carbon cost represents less than 10% of the projected cost of the completed catalyst.

Sensitivity Case Economics

Much of the cost benefit seen for the two oxidation catalyst technologies in Table 2 is derived from the assumption that there are significant fly ash revenues that would be lost if activated carbon injection is employed for mercury control. Therefore, a sensitivity case was run for the other extreme, where all of the fly ash is currently disposed of in a landfill, perhaps blended with the FGD byproduct for co-disposal. The results of this sensitivity case are summarized in Table 3. The results in the table show that the first-year costs for the oxidation catalyst technologies would be nearly equal to that of activated carbon injection if the catalysts are replaced every two years and the plant does not sell any of its fly ash.

Table 3. Comparison of Sensitivity Case Economics for Mercury Control Technologies – No Fly Ash Sales

Parameter	FGD Carbon Injection	Palladium-based Oxidation Catalyst	C #6 Oxidation Catalyst
Capital Equipment, $1000	$2,213	$1,289	$1,289
Catalyst Cost, $1000	-	$5,360*	$5,218**
Delivered Carbon Cost, $1000/yr	$3,109	-	-
Lost Fly Ash Sales, $1000/yr	-	-	-
Increased Landfill Disposal Costs, $1000/yr	$9	-	-
Subtotal O&M Costs, $1000/yr	$3,118	-	-
Capital Equipment Amortization, $1000/yr	$266	$155	$155
Catalyst Amortization Costs, $1000/yr	-	$3,006	$2,926
Total First-year Costs, $1000/yr	$3,384	$3,161	$3,081
First-year Cost, % of Activated Carbon Cost	-	93	91

*Includes delivery, installation, and disposal costs
**Includes delivery, installation, and disposal costs; value shown is based on the low end of the $710/ft^3 to $860/ft^3 projected catalyst cost

Results presented in the previous Quarterly Technical Progress Report[6] showed that the palladium-based catalyst could be regenerated by exposure to heated air. Within the limitations of the test conducted, the C #6 catalyst did not regenerate, though. Therefore, another sensitivity case was run, illustrating the effects of catalyst regeneration on oxidation catalyst economics, but only for the palladium catalyst. Sensitivity cases were run both with and without fly ash sales being considered.

Little is known about what minimum conditions (temperature and exposure time) are needed to regenerate the palladium catalyst, how long regenerated catalyst will remain active relative to the activity of fresh catalyst, and how many times a catalyst can be regenerated before it must be replaced. Consequently, it was not feasible to develop a detailed estimate for catalyst regeneration economics. Instead, two simplifying assumptions were made. One was that the regenerated catalyst could be regenerated once, after two years in service, then would be discarded after a total of four years of service. The other was that the costs associated with regeneration could be represented as an annual cost, and expressed as a percentage of the original catalyst cost. For these sensitivity cases, factors of 5% and 10% were used.

For the palladium catalysts, these regeneration cost factors result in annual charges of $268,000 and $536,000, respectively. These dollar amounts are seen as being relatively conservative, considering they are levied as an annual expense in these economics, while only one regeneration would occur in four years. Also, to put these dollar amounts into perspective, the labor associated with removing and reloading the catalyst modules to effect this regeneration is estimated at less than $200,000, while the fuel cost required to heat the regeneration air was estimated at less than $20,000 per regeneration.

Table 4 presents the results of the regeneration cases for the palladium-based catalyst. Cases with and without fly ash sales are shown, at both factor levels for regeneration costs. The results show that regeneration would markedly improve oxidation catalyst technology economics. In the case where the plant sells its fly ash, the first-year cost for the oxidation catalyst technology with regeneration ranges from 58% to 62% less than the activated carbon estimate. Where the plant is not selling its fly ash, regeneration improves the process economics to the point where oxidation catalyst technology is 32 to 40% less costly than activated carbon injection rather than being almost equal in estimated cost.

These results underscore the importance of regeneration to the process economics. In future process development efforts, more emphasis will be placed on determining minimum requirements for regenerating the palladium and other catalysts, and on determining the active life of regenerated catalysts. The results also show that, unless there is a technology breakthrough which lowers the cost of producing the C #6 catalyst, it does not represent a significant potential as a lower cost catalyst compared to palladium.

Table 4. Comparison of Sensitivity Case Economics for Mercury Control Technologies – Palladium Catalyst with Regeneration

Parameter	With Fly Ash Sales		Without Fly Ash Sales	
	Lower Regeneration Cost Factor*	Higher Regeneneration Cost Factor*	Lower Regeneration Cost Factor*	Higher Regeneration Cost Factor*
Capital Equipment, $1000	$1,289	$1,289	$1,289	$1,289
Catalyst Cost, $1000	$5,360**	$5,360**	$5,360**	$5,360**
Regeneration Cost, annual factor, $1000	$268	$536	$268	$536
Capital Equipment Amortization, $1000	$155	$155	$155	$155
Catalyst Amortization Costs, $1000	$1,618	$1,618	$1,618	$1,618
Total First-year Costs, $1000	$2,041	$2,309	$2,041	$2,309
Corresponding Activated Carbon First-year Costs, $1000	$5,435	$5,435	$3,384	$3,384
First-year Cost, % of Activated Carbon Cost	38	42	60	68

*Lower regeneration cost factor is 5% of initial catalyst cost, higher factor is 10%
**Includes delivery, installation, and disposal costs

Pilot Unit Operation at Spruce Plant

Background

The pilot unit was started up at Spruce Plant in late August 2003 and operated with the Pd #1 and gold (Au) catalysts installed for most of the month of September. The host unit came off line for a fall outage the evening of September 26, and the outage continued until October 27. The two remaining catalysts (SCR and C #6) were installed in the pilot unit and the pilot unit was restarted on November 13. The unit has operated continuously with all four catalysts on line since then.

Pilot unit inlet and catalyst outlet mercury concentration data were first collected for all four catalysts at Spruce the week of December 8, 2003. SCEM relative accuracy tests by the Ontario Hydro Method were conducted at the same time. The week of January 5, 2004, two SCEMs were taken to the site and used to measure flue gas total mercury and elemental mercury concentrations at the fabric filter inlet and outlet, and at the wet FGD outlet locations on the host unit. These measurements were made to develop a baseline characterization of host unit flue gas mercury conditions prior to rebagging the fabric filter with new bags. The rebagging began on January 12, 2004. Routine catalyst activity measurements by Hg SCEM were made on February 13, 2004, after 11 of the 14 compartments in the west fabric filter (directly upstream of the catalyst pilot unit) had been rebagged. The rebagging was completed at the end of February. Subsequent catalyst activity measurements were made in made in May and August 2004. These results have all been reported previously. During the current quarter, catalyst activity measurements were made across all four catalysts by mercury SCEM and by the Ontario Hydro Method.

Catalyst Pressure Drop Results

The pressure drop across the four catalyst chambers at Spruce remained nearly constant between 0.2 and 0.3 in H_2O during the current quarter. It does not appear that sonic horns will be required to prevent fly ash buildup, most likely because a high-efficiency reverse-gas fabric filter is used for particulate control at this site. The use of a fabric filter results in a low dust loading in the pilot unit inlet flue gas, and a dust loading that has less residual electrostatic charge than would flue gas downstream of an ESP.

Catalyst Activity Results

One set of catalyst measurement trip results are presented in this report, from October 2004. These results are shown in Table 5. As has been previously reported, the measurements at the pilot unit inlet showed high mercury oxidation percentages, with SCEM measurements showing 60% to 80% oxidized rather than the expected 20 to 30% oxidized mercury typical of PRB flue gases. This effect appears to be an influence of the fabric filter used for particulate control at Spruce. The fabric filter operates at a low air-to-cloth ratio (less than 1.5 acfm/ft^2) and at flue gas temperatures below 300^{o}F.

Note that on this trip, the performance of each catalyst was measured on individual days, rather than all on a single day as on most previous measurement trips. The day-to-day measurements illustrate how variable the baghouse outlet/catalyst inlet total mercury and mercury oxidation are at Spruce Plant. Total mercury concentrations varied from 8.1 to 13.8 μg/Nm^3, and the mercury oxidation percentages varied from 60 to 80%. The resulting catalyst inlet elemental mercury concentrations varied by more than a factor of two, from 1.6 to 3.9 μg/Nm^3. During the previous catalyst activity measurements at Spruce in August, the mercury oxidation percentage at the baghouse outlet/catalyst inlet averaged even higher at 92%, and the inlet elemental mercury concentration was even lower at only 1.25 μg/Nm^3.

These variations are presumably due to variations in the coal mercury content, and/or baghouse operation. For example, baghouse cleaning cycles may impact baghouse outlet mercury concentration and speciation, as the “dirty” bags may adsorb and/or oxidize more mercury than just-cleaned bags. Regardless of the cause, the observed day-to-day and trip-to-trip variability in mercury concentrations underscores the need to simultaneously measure the inlet and outlet mercury concentrations when evaluating catalyst performance at Spruce.

Table 5. August Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM)

Location	Date	Total Hg (mg/Nm^3, corrected to 3% O_2)*	Elemental Hg (mg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst, %	Apparent Hg^0 Oxidation Across Catalyst, %	Overall Hg Oxidation Percentage
Pd #1 Inlet	Oct. 19	10.7	2.7	-	-	75
Pd #1 Outlet	Oct. 19	12.1	0.6	0	76	95
C #6 Inlet	Oct. 21	13.8	3.4	-	-	75
C #6 Outlet	Oct. 21	10.4	0.7	24	80	94
Au Inlet	Oct. 20	9.7	3.9	-	-	60
Au Outlet	Oct. 20	10.0	0.3	0	92	97
SCR Catalyst Inlet	Oct. 22	8.1	1.6	-	-	80
SCR Catalyst Outlet	Oct. 22	9.1	1.0	0	41	89

*Note: 1.00 µg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

The October data suggest that the catalysts adsorb and desorb mercury as the inlet flue gas total mercury concentration varies. For example, on October 21 the inlet total mercury was measured at 13.8 µg/Nm^3, considerably higher than the value of 9.7 µg/Nm^3 measured the day before. On October 21, the catalyst outlet total mercury was measured to be lower than at the inlet, at 10.4 µg/Nm^3, indicating some mercury adsorption across the catalyst. The next day, the catalyst inlet total mercury was down to 8.1 µg/Nm^3, and the outlet was higher at 9.1 µg/Nm^3. This suggests that the catalyst was desorbing some of the mercury adsorbed the day before while treating flue gas with a significantly higher total mercury concentration. This effect is not surprising, since adsorption is typically a function of the partial pressure of the adsorbing species in the gas contacting the adsorbing solids.

These data also show a correlation between catalyst inlet elemental mercury concentration and mercury oxidation percentage across the catalyst being evaluated on that day. For example, the best performing, gold catalyst saw an inlet elemental mercury concentration of 3.9 µg/Nm^3, while the poorest performing, SCR catalyst saw an inlet concentration of only 1.6 µg/Nm^3. However, this appears to be only a coincidence, as such an effect was not seen in the previous, May 2004 data, where two analyzers were also used to simultaneously measure the inlet and outlet elemental mercury concentrations for each catalyst.

All of the catalyst activity results from Spruce since September 2003 are plotted in Figure 1. The early catalyst activity results show quite a bit of variability over time, and during some measurement periods the mercury oxidation percentages were much lower than expected. The more recent data, from the May, August and October measurement trips, are believed to be more reliable because more sensitive atomic absorption detectors were used in the Hg SCEMs.

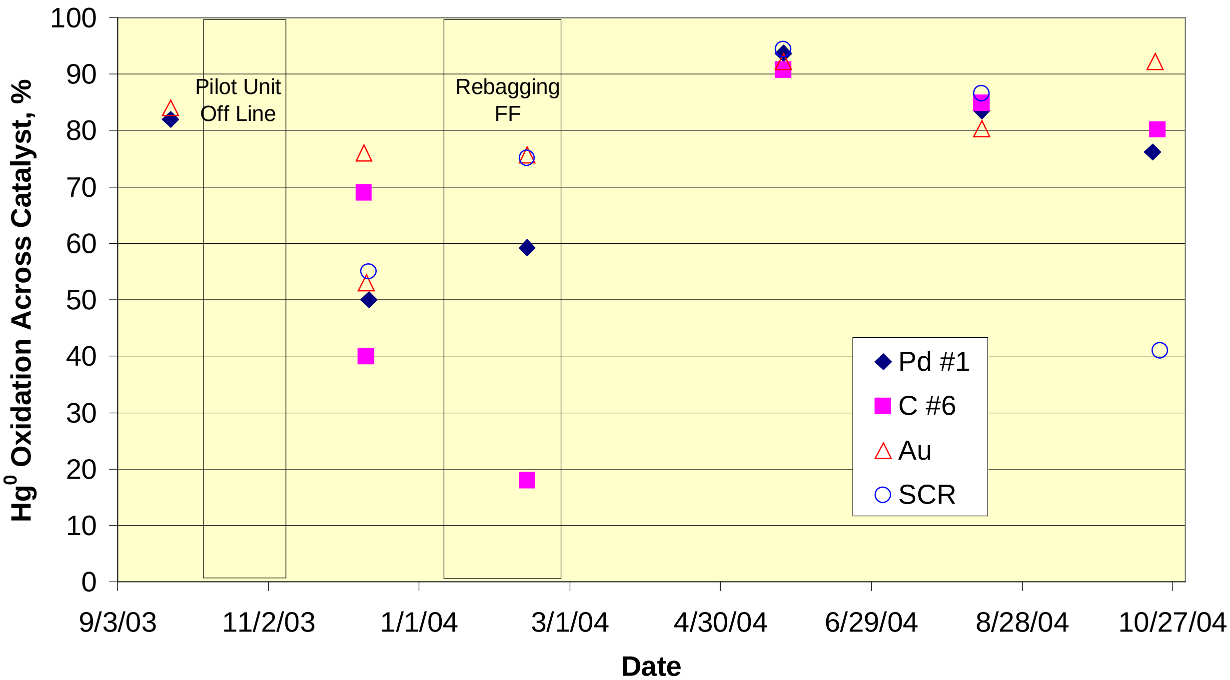

Figure 1. Catalyst Activity Versus Time in Service at Spruce Plant

The May through October data show that three of the four catalysts are achieving greater than 75% oxidation of the inlet elemental mercury. The most recent, October data show that the fourth catalyst, the SCR catalyst, has seen a dramatic drop in mercury oxidation activity, down to 41% oxidation across the catalyst in October from nearly 87% in August. The data for three of the four catalysts show a downward trend in measured activity over the time period of May through October, with the Pd #1 and C #6 catalysts seeing a linear decrease with time while the SCR catalyst saw an abrupt decrease in the last set of measurements. Only the gold catalyst data show no tendency for loss of activity versus time, with the October data equaling the performance measured in May and improving over the performance measured in August. The next (and final) measurement trip is scheduled for early February 2005, and will provide an opportunity to see whether the activity trends measured in May through October will continue.

Ontario Hydro Relative Accuracy Tests

The week after catalyst activity tests were conducted, a second week of testing was conducted, including Hg SCEM relative accuracy tests by the Ontario Hydro method. Both weeks of testing were in conjunction with pilot wet FGD tests conducted as part of project DE-FC26-04NT41992.

The results from the Ontario Hydro relative accuracy tests are summarized in Table 6. The pilot wet FGD data are presented in the Quarterly Technical Progress Report for that project.

Table 6. October 2004 Ontario Hydro Relative Accuracy Results for Spruce Pilot (mean and 95% confidence interval of three runs compared to simultaneous Hg SCEM results)

	Total	Elemental	Oxidized
Pd #1, October 26, 2004			
Catalyst Inlet – OH, μg/Nm^3*	5.0 ± 4.1	0.5 ± 0.1	4.5 ± 4.1
Catalyst Inlet - SCEM, μg/Nm^3	6.0 ± 0.8	0.9 ± 0.8	5.3 ± **
Relative Accuracy, % (based on means)	20	80	18
Catalyst Outlet - OH, μg/Nm^3	5.7 ± 3.7	0.5 ± 0.2	5.2 ± 3.5
Catalyst Outlet - SCEM, μg/Nm^3	6.1 ± 2.3	0.6 ± 0.5	5.5 ± 1.8
Relative Accuracy, % (based on means)	7	18	6
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	7	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	39	-
C #6, October 28, 2004			
Catalyst Inlet - OH, μg/Nm^3	9.1 ± 3.1	0.8 ± 0.5	8.3 ± 3.2
Catalyst Inlet - SCEM, μg/Nm^3	8.4 ± 1.0	0.7 ± **	7.1 ± **
Relative Accuracy, % (based on means)	-8	-13	-15
Catalyst Outlet - OH, μg/Nm^3	10.4 ± 0.4	0.4 ± 0.4	10.0 ± 0.2
Catalyst Outlet - SCEM, μg/Nm^3	6.2 ± 0.1	1.1 ± 0.3	5.2 ± 0.2
Relative Accuracy, % (based on means)	-40	167	-48
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	50	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	-52	-
Gold, October 27, 2004			
Catalyst Inlet – OH, μg/Nm^3	12.0 ± 1.7	3.0 ± 0.6	8.9 ± 1.2
Catalyst Inlet - SCEM, μg/Nm^3	8.9 ± 3.2	2.7 ± 0.7	6.2 ± 3.2
Relative Accuracy, % (based on means)	-26	-11	-31
Catalyst Outlet - OH, μg/Nm^3	10.3 ± 3.1	0.4 ± 0.3	10.0 ± 2.8
Catalyst Outlet - SCEM, μg/Nm^3	10.9 ± 0.9	1.0 ± 0.4	10.0 ± 0.5
Relative Accuracy, % (based on means)	6	164	0
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	88	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	64	-
SCR Catalyst, October 29, 2004			
Catalyst Inlet – OH, μg/Nm^3	7.9 ± 1.5	1.0 ± 0.8	6.9 ± 2.2
Catalyst Inlet - SCEM, μg/Nm^3	7.2 ± 1.5	0.4 ± 0.0	6.4 ± 2.3
Relative Accuracy, % (based on means)	-9	-60	-8
Catalyst Outlet - OH, μg/Nm^3	7.9 ± 2.4	0.2 ± 0.1	7.7 ± 2.4
Catalyst Outlet - SCEM, μg/Nm^3	7.7 ± 1.5	0.6 ± 0.2	6.9 ± 2.6
Relative Accuracy, % (based on means)	-2	260	-11
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	83	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	50	-

*****Note – All concentrations corrected to 3% O_2, dry basis; 1 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input
**Hg SCEM data were available for only one of the three OH runs, so 95% confidence interval could not be calculated

The Hg SCEM results from this second week were not reported previously in Table 5 and Figure 1 for two reasons. One is that, because of sampling port configurations, it was not possible to sample the catalyst inlet and outlet locations simultaneously with two Hg SCEMs during the Ontario Hydro method sampling. As described previously, this makes any oxidation data measurements suspect because of the observed variability in total and elemental mercury concentrations at the Spruce baghouse outlet/oxidation catalyst pilot unit inlet.

The second reason the results from the second week were not included above is that during the second week, a heater on the inertial gas separator (IGS) filter used to extract a particulate-free sample into the impinger train for the Hg SCEM failed. Although the sampling crew attempted to compensate for this failure by wrapping the IGS filter with heat tape and insulation, the IGS filter temperature remained at about 270^{o}F, which is well below the desired temperature of 400^{o}F. Although the SCEM results from the second week do not show clear signs of measurement bias, they remain suspect.

As was seen the week before and reported in Table 5, the flue gas total and elemental mercury concentrations also varied considerably from day to day in the results presented in Table 6. As measured by the Ontario Hydro method, the catalyst pilot unit inlet total mercury concentrations varied from 5.0 to 12.0 $\mu g/Nm^3$, a factor of more than two. The inlet elemental mercury concentrations varied from 0.5 to 3.0 $\mu g/Nm^3$, a factor of six.

Because of the observed variability in concentrations, the table shows the mean value for three runs (sometimes fewer than three for the Hg SCEM as discussed below) as well as the 95% confidence interval of the mean. The magnitude of the 95% confidence interval can be compared to the mean value to provide a measure of the variability of the measurements. The larger the 95% confidence interval relative to the mean value, the more variable were the measurement results. This variability could be due to changes in the actual flue gas concentrations over time, variability within the measurement methods, or both.

Since the Hg SCEM measurements were made with only one analyzer, this meant that four measurements had to be made (catalyst inlet and outlet, total and elemental mercury) while the two Ontario Hydro trains (catalyst inlet and outlet) completed each two-hour run. Thus, the Hg SCEM data for each of the four measurements represent, at best, 20 to 30 minutes of data collected at different times during the Ontario Hydro runs while the Ontario Hydro results represent an integrated sample collected over the entire two hours. Furthermore, because of the IGS filter heating issues discussed above, for some Ontario Hydro run periods, all four Hg SCEM measurements were not completed, as time was lost trying to get the IGS filter up to temperature. Since the oxidized mercury concentration is measured by the difference between total and elemental mercury with the Hg SCEM, this meant that any time a total or elemental mercury concentration was not measured at either the catalyst inlet or outlet, the oxidized mercury concentration could not be calculated either. Thus, for some Ontario Hydro mean values in Table 6, each of which represents three runs, the Hg SCEM data may only correspond with one or two of those Ontario Hydro runs. The ones with only one set of SCEM data are noted in the table, as a 95% confidence interval could not be calculated from only one value.

Comparing the Ontario Hydro method results to Hg SCEM results, the catalyst inlet and outlet total mercury measurements agreed well for all but two sets of data: the catalyst inlet on October 27 (gold catalyst) and the catalyst outlet on October 28 (C #6 catalyst). In the case of the inlet on October 27, the disagreement may be due to the observed high variability of the inlet total mercury concentrations. When the 95% confidence intervals about the means for the two measurement methods are compared, they overlap considerably. For the outlet of the C #6 catalyst on October 28, there is apparently some bias between the two methods, as the 95% confidence intervals are relatively small for the mean values by both methods and the two 95% confidence intervals about the means do not come close to overlapping.

For the elemental mercury concentration measurements, the catalyst inlet concentration data agree reasonably well between the two methods, particularly when the 95% confidence intervals about the mean values are considered. On the days where the mean values differed significantly, the confidence intervals were large for one or more method, so the 95% confidence intervals for the means by the two methods overlapped in each case.

For the catalyst outlet elemental mercury measurements, the bias previously seen at CCS appears to be present in these results: in general, the Ontario Hydro method measures lower elemental mercury concentrations at the oxidation catalyst outlet locations than does the Hg SCEM. For some of the measurements, though, the apparent bias is within the 95% confidence intervals of the mean values for the two methods.

For oxidized mercury concentrations, the two methods agreed well except for the two measurements where the SCEM results for total mercury concentration appeared to be biased low relative to the Ontario Hydro results: the catalyst inlet on October 27 (gold catalyst) and the catalyst outlet on October 28 (C #6 catalyst). Since the SCEM measures oxidized mercury concentrations as the difference between the total and elemental mercury concentrations, this apparent bias was carried over to the oxidized mercury concentration by the SCEM method. As with the total mercury data, for the October 27 data the difference between the two methods may be explained by data variability (large 95% confidence intervals), but this is not the case for the October 28 data.

Table 6 also shows observed oxidation percentages across the catalysts. For three of the four days, the mean catalyst inlet elemental mercury concentrations were 1 $\mu g/Nm^3$ or lower. A number of the individual run results at the catalysts' inlet and outlet showed elemental mercury concentrations below 0.5 $\mu g/Nm^3$, the stated lower measurement limit of the Ontario Hydro Method.[8] Consequently, for the three catalysts tested on these days (Pd #1, C #6 and SCR) the Ontario Hydro results may not be valid. Based on past experience at Spruce, the Hg SCEM does not appear to be able to successfully measure catalyst oxidation performance when the inlet elemental mercury concentration is below 1 $\mu g/Nm^3$. The mean elemental mercury oxidation percentages across these three catalysts range from 18 to 83% by the Ontario Hydro Method and from –52 to +50% by Hg SCEM. None of these results are believed to be valid.

For the gold catalyst, the mean inlet elemental mercury concentration was about 3 $\mu g/Nm^3$, which should be high enough to allow measurement of catalyst performance. The mean percent oxidation across the gold catalyst was 88%, which is in good agreement with the 92% value measured simultaneously with two Hg SCEMs the week before. The mean value for the Hg SCEM data was 64% oxidation, which is well below the 92% value measured the week before. However, as stated previously the Hg SCEM data in Table 6 were measured with only one analyzer, which makes catalyst performance measurement difficult due to observed variability in inlet flue gas elemental mercury concentrations. When the 95% confidence intervals of the Hg SCEM data are considered, the 95% confidence interval of the mean oxidation percentage calculated from those values ranges from 30% to 84%, the latter of which approaches the performance measured the week before.

CONCLUSION

The catalyst activity versus time data from CCS were used to develop comparative economics for the oxidation catalyst technology and a more conventional activated carbon injection approach, both for a scrubbed plant that fires North Dakota lignite and that must achieve at least 55% additional mercury capture. These comparative economics showed that for a plant that currently sells its fly ash, oxidation catalyst technology could achieve greater than 55% increased mercury control at a cost about 40% less than by injecting Norit FGD activated carbon. This assumes the catalyst is used two years then discarded. However, if the plant does not currently sell its fly ash, the activated carbon case was approximately the same cost as the catalyst technology.

Regeneration can greatly improve the cost effectiveness of the oxidation catalyst technology. Although regeneration costs could not be definitively estimated, sensitivity cases were run using two different estimated regeneration cost values. These cases showed that for a plant that currently sells its fly ash, regenerating the palladium catalyst once, to allow it to remain in service for a total of four rather than two years, improved the process economics to where oxidation catalyst technology costs were about 60% lower than activated carbon injection costs. Even in the case where the plant does not sell its fly ash, the regeneration scenario improved the economics of the oxidation catalyst technology to the point where it was estimated to be 30 to 40% lower in cost than activated carbon injection as opposed to nearly equal in cost without regeneration.

These cost estimates allow two conclusions to be drawn from the results at CCS. One is that, based on current cost estimates for producing commercial quantities of the C #6 catalyst, it does not appear to be significantly less costly than the palladium catalyst. This is in spite of the fact that palladium is over 1000 times the cost of the C #6 raw carbon material on a mass basis. The second conclusion is that regeneration will be very important to the future economics of this developing mercury control technology.

These two conclusions raise the question as to whether development resources should continue to be invested in the experimental, C #6 catalyst, or whether more emphasis should be placed on developing regeneration technology for palladium-based catalysts (and/or gold catalysts as are being tested at Spruce Plant). However, given the site specificity seen in catalyst performance in previous, smaller-scale catalyst tests, it remains worthwhile to continue to test as wide a range of catalyst types as possible at pilot scale.

At the Spruce site, the fabric filter upstream of the pilot unit has had two implications on the pilot testing. One is that is does not appear that sonic horns will be required to keep fly ash from accumulating within the catalyst cells. The other implication is that the fabric filter oxidizes a high percentage of the elemental mercury in the air heater outlet flue gas, so the inlet gas to the pilot unit contains relatively low elemental mercury concentrations (typically 1 to 4 $\mu g/Nm^3$). This makes evaluation of catalyst performance difficult, as it is difficult to quantify flue gas elemental mercury concentrations that are well below 1 $\mu g/Nm^3$.

Based on results from October, three of the four catalysts (Au, C #6, and Pd #1 catalysts) are achieving greater than 75% elemental mercury oxidation in this PRB flue gas, typically lowering catalyst outlet elemental mercury concentrations well below 1 $\mu g/Nm^3$. One catalyst, the SCR catalyst, was measured to have seen a dramatic drop in oxidation activity, down to 41% elemental mercury oxidation in October. During the upcoming quarter, final site measurements will be conducted to determine whether these catalyst activity trends will continue.

Ontario Hydro relative accuracy test results from October 2004 show reasonably good agreement with the Hg SCEM for total mercury concentrations, and for mercury speciation at the catalyst inlets. For the catalyst outlet, the Ontario Hydro method results showed lower mean elemental mercury concentrations than the Hg SCEM results. A similar bias was seen during previous Ontario Hydro relative accuracy tests in at CCS in July 2003 and June 2004. At CCS, the project team felt the evidence points to the measurement bias being with the Ontario Hydro method rather than the Hg SCEM, although it is not clear what about these catalysts produces such a bias. However, for these recent Spruce results, the observed bias may be due to measurement issues with the Hg SCEM, including a low IGS filter temperature and the fact that only one Hg SCEM had to be used to collect both catalyst inlet and outlet data during each Ontario Hydro run.

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